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Synthesis of Orcinol Monomethyl Ether*

By

Kazuo ADACHI

Department of Applied Chemistry
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Abstract

Orcinol monomethyl ether, a constituent of oak moss oil, was synthesized from *m*-cresol *via* the processes of bromination, nitration, and reduction. A synthetic intermediate, 2, 4, 6-tribromo-3-methylanisole [2] was nitrated with a mixed acid to give its nitro derivative along with a benzoquinone derivative as a by-product. Orcinol monomethyl ether [8] was obtained by hydrolyzing the diazotized 3-methoxy-5-methylaniline [7], and some azo compounds [9], [10], and [11] were synthesized from the diazonium salt of [7]. Bromination and subsequent nitration of resorcinol were also investigated.

I. Introduction

The essential oil of oak moss (*Evernia prunastri* Ach.) has been used to prepare the compound perfumes as a blender or a fixative in the perfume industry. This mossy note oil is an important component of chypre or fougere note perfumes, which are utilized for cosmetics snch as eau de Cologne, lotion, and toilet soap. Orcinol monomethyl ether (3-methoxy-5-methylphenol) is a constituent of oak moss oil and has been used to prepare artificial oak moss oil and the compound perfumes.

Orcinol (3,5-dihydroxytoluene, 5-methylresorcinol) was prepared by decardoxylation of orsellic acid, which was isolated as its derivatives from lichens such as *Roccella* and *Lecanora* species. The synthesis of orcinol has been effected by the condensation of ethyl acetoacetate with ethyl crotonate.[1] The methylation of orcinol by refluxing with dimethyl sulfate and K_2CO_3 in acetone afforded orcinol dimethyl ether, which was partially demethylated with sodium ethanethiolate to give orcinol monomethyl ether.[2]

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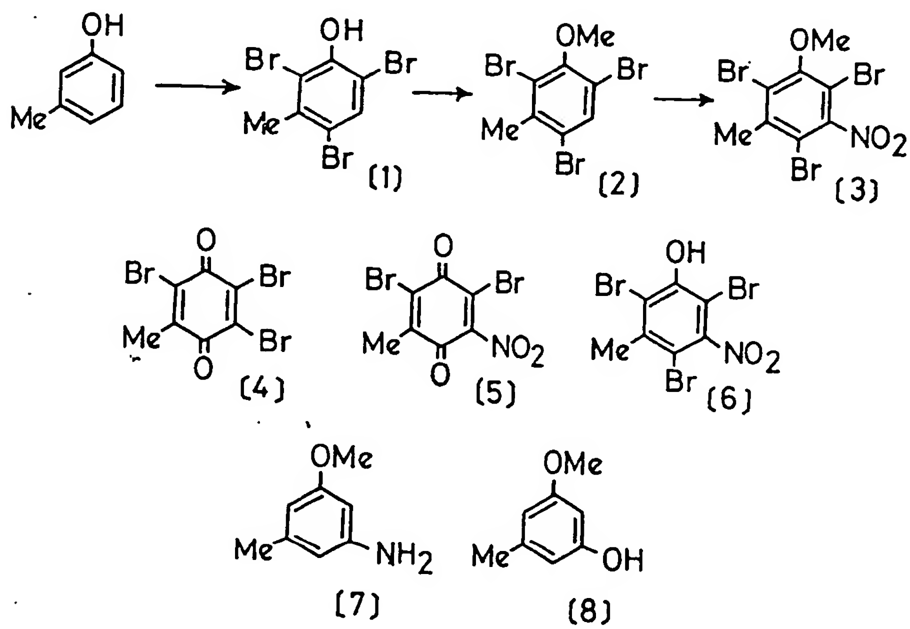
In this paper, starting from *m*-cresol the synthesis of orcinol monomethyl ether through bromination successive nitration will be described. Some azo compounds were also synthesized from 3-methoxy-5-methylaniline, an intermediate of orcinol monomethyl ether. Futhermore, similar reactions using resorcinol were attempted as an alternative synthetic route to the title compound from resorcinol.

II. Results and Discussion

1. Synthesis of Orcinol Monomethyl Ether 〔8〕 from *m*-Cresol.

Orcinol monomethyl ether 〔8〕 was synthesized through 3-methoxy-5-methylaniline 〔7〕 from *m*-cresol as follows.



Bromine was rapidly added to a suspension of *m*-cresol in water to give 2,4,6-tribromo-3-methylphenol 〔1〕 in the theoretical amount, but adding bromine more slowly brings about a lower yield of 〔1〕 as a result of increase in NaOH insoluble matter. A solution of the sodium salt of 〔1〕 in water was methylated with dimethyl sulfate to give a good yield of 2,4,6-tribromo-3-methylanisole 〔2〕.

Nitration of 〔2〕 with a mixed acid yielded a product having mp 103～217℃, which was a mixture consisting of 2,4,6-tribromo-3-methyl-5-nitroanisole 〔3〕 (mp 126～127℃) and 3,5,6-tribromo-2-methyl-1,4-benzoquinone 〔4〕 (mp 233～234℃). During the reaction, a portion of 〔2〕 was subjected to migration of a bromine atom followed by oxidation with nitric acid to give the benzoquinone 〔4〕, which was no longer affected by the mixed acid. A mixture of 〔4〕, 2,4-dinitrophenylhydrazine

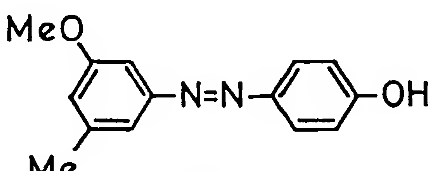
and H_2SO_4 in ethanol afforded the dinitrophenylhydrazone of acetaldehyde, but did not yield that of [4]. This result indicates that ethanol was oxidized with [4], a similar dehydrogenating agent as chloranil and DDQ, to provide acetaldehyde, but the hydroquinone corresponding to [4] could not be isolated from the reaction mixture. The reaction of [3] with a mixed acid afforded 3,5-dibromo-2-methyl-6-nitro-1,4-benzoquinone [5] (mp 201~202℃), which was decomposed by refluxing in methanol. IR spectrum of [5] had the carbonyl absorption at 1680, 1660 cm^{-1} and the absorption due to the nitro group at 1545, 1360 cm^{-1}, though that of [4] failed the latter.

In his previous paper,[3] the author reported that 2,4-dibromo-5-methylanisole was refluxed with HI in acetic acid to yield *m*-cresol as a result of demethylation and debromination. When [3] was refluxed with HI, however, the reaction product was only 2,4,6-tribromo-3-methyl-5-nitrophenol [6]. By refluxing with Zn in 38% HCl, [3] was debrominated successively and reduced to give 3-methoxy-5-methylaniline [7]. The acetyl derivative of [7] showed mp 120~121℃, but mp 110~111 ℃ in the paper.[4]

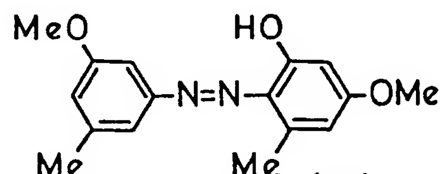
Orcinol monomethyl ether [8] was obtained by refluxing the diazonium salt of [7] in dil H_2SO_4. In the NMR spectrum, three aromatic protons of [8] showed a broad signal.

2. Azo Compounds Prepared from 3-Methoxy-5-methylaniline [7].

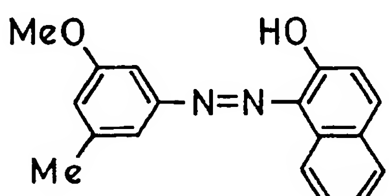
Three monoazo compounds [9], [10] and [11] were synthesized from the diazonium salt of [7] by coupling with phenol, orcinol monomethyl ether, and β-naphthol, respectively.



[9]



[10]



[11]

The spectral data of these azo compounds are shown in Table 1. In general,

phenol is coupled at its *p*-position with a diazonium compound to form an azo linkage, and *β*-naphthol is at *o*-position of the hydroxyl group. Table 1 indicates that the hydroxyl group of [9] has an absorption band at 3100 cm^{-1} in IR and a broad signal at δ 5.62 in NMR, and the hydroxyl group of [11] is hydrogen-bonded with the azo linkage having an absorption at 3450 cm^{-1} (IR) and a signal at δ 16.00 (NMR). Therefore, the structure [10] was proposed to the azo compound prepared from orcinol monomethyl ether [8], *i. e.*, [8] was also coupled at *o*-position of its hydroxyl group with the diazonium salt of [7].

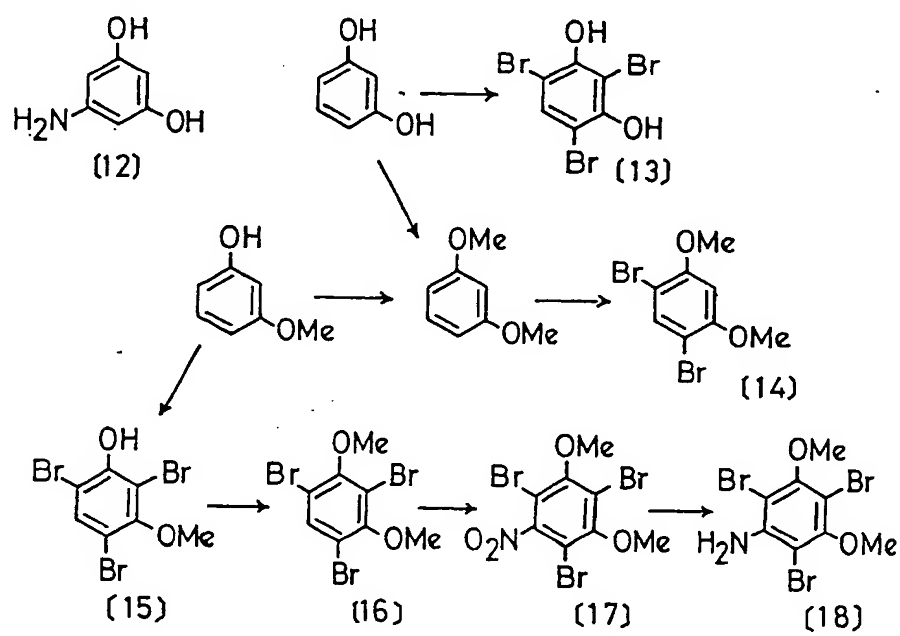
Table 1. IR and NMR spectra of the azo compounds [9], [10] and [11].

Azo compounds	IR (cm^{-1}) O−H	IR (cm^{-1}) −N=N−	NMR (δ) O−H
[9]	3100	1595	5.62
[10]	3450	1525	11.32
[11]	3450	1510	16.00

3. Bromonitroresorcinol Dimethyl Ether.

The synthesis of 5-aminoresorcinol [12] was attempted. This is expected to be an intermediate leading to orcinol from resorcinol.

Resorcinol and its methyl ethers were brominated successively and nitrated in the same way as the synthesis of [7] from *m*-cresol, but neither [12] nor its methyl



ether yields in this way.

The bromination of resorcinol in aqueous solution gave a good yield of tribromoresorcinol [13], which was dissolved in NaOH or $NaHCO_3$ solution and the resulting dark solution yielded only tarry material after acidification with HCl, but no original bromoresorcinol.

The reaction of resorcinol dimethyl ether with 3 mol of bromine in water gave the dibromo derivative [14], but not the tribromo derivative [16]. Tribromoresorcinol dimethyl ether [16] was prepared by methylation of tribromoresorcinol monomethyl ether [15], which was obtained from resorcinol monomethyl ether by bromination.

The nitration of [16] afforded 2, 4, 6-tribromo-5-nitroresorcinol dimethyl ether [17], which was reduced with Zn and conc HCl at room temperature to give 2, 4, 6-tribromo-3, 5-dimethoxyaniline [18]. When a mixture of [17], Zn and conc HCl was refluxed, the reaction product was only tar.

III. Experimental

1. 2,4,6-Tribromo-3-methylanisole [2].

To a mixture of 21.6g (0.2 mol) of *m*-cresol and 200 ml water, 102g (0.64 mol) of bromine was added at 10°C for 10 min with stirring and the mixture was then stirred at 40°C for 40 min. Excess bromine was removed with Na_2SO_3, and the precipitated crystals were filtered giving 69.0g (100%) of 2, 4, 6-tribromo-3-methylphenol [1], woolly crystals from methanol; mp 82~83°C (lit,[3] mp 81.5~82.5°C).

To a solution of 138.0g (0.4 mol) of [1] in 410g (0.44 mol) of 4.3% NaOH, 52.8g (0.42 mol) of dimethyl sulfate was added at 10°C, and the reaction mixture was stirred at 90°C for 2 h. The excess reagent was destroyed by stirring with 35 ml of 28% NH_3 at 90°C for 30 min. The precipitated crystals, after cooling, were filtered to give 134.2g (93.5%) of 2,4,6-tribromo-3-methylanisole [2], needles from methanol, mp 75.5~76.5°C (lit,[3] mp 75.5~76.5°C). Acidification of the filtrate freed from [2] afforded 3.9g (2.8%) of the unreacted [1].

2. 2,4,6-Tribromo-3-methyl-5-nitroanisole [3].

To a mixed acid prepared from 18.0g of 98% H_2SO_4 and 4.7g (73 m mol) of 98% HNO_3, 18.0g (50 m mol) of 2, 4, 6-tribromo-3-methylanisole [2] was added at 40°C for 15min. After stirring at 60°C for 30 min, the reaction mixture was poured into 300 ml ice water, and the yellow granular product was filtered, 18.1g (89.4%), mp 103~217°C.

The crude nitro compound was refluxed in 30 ml methanol for 3 h. The methanol solution and a few crystals of a by-product were decantated from the mixture, remaining 15.2 g (75.2%) of 2, 4, 6-tribromo-3-methyl-5-nitroanisole [3], prisms from methanol, mp 126~127°C. Found: C, 23.92; H, 1.39; N, 3.46%. Calcd for $C_8H_6Br_3NO_3$:

C, 23.79; H, 1.50; N, 3.47%.

IR: 1540, 1445, 1385, 1350, 1280, 1240, 1160, 955, 925, 780, 675 and 640 cm^{-1}.

3. 3,5,6-Tribromo-2-methyl-1,4-benzoquinone 〔4〕.

By fractionally recrystallizing the crude nitro compound of 〔2〕, 1.1 g (6.2%) of 3,5,6-tribromo-2-methyl-1,4-benzoquinone 〔4〕 was obtained as a by-product, yellow leaves from ligroin, mp 233~234℃. Found: C, 23.52; H, 0.76%. Calcd for $C_7H_3Br_3O_2$: C, 23.43; H, 0.84%.

IR: 1680, 1660, 1565, 1280, 1235, 1135, 985, 705 and 680 cm^{-1}.

The benzoquinone 〔4〕 was treated with a mixed acid, recovering only the starting material. A mixture of 1.0 g of 〔4〕 and 1.0 g of 98% H_2SO_4 in 100 ml ethanol was refluxed for 10 h and distilled. The resulting distillate (85 ml) was allowed to react with a reagent prepared from 0.8 g of 2,4-dinitrophenylhydrazine, 2 g of 98% H_2SO_4, and 10 ml ethanol giving 1.1 g of acetaldehyde 2,4-dinitrophenylhydrazone, yellow needles from ethanol, mp 147~148℃. Found: C, 42.91; H, 3.48; N, 25.26%. Calcd for $C_8H_8N_4O_4$: C, 42.86; H, 3.60; N, 24.99%.

A solution of 〔4〕 and 2,4-dinitrophenylhydrazine in ethanol was refluxed to give the hydrazone of acetaldehyde, but not that of 〔4〕.

4. 3,5-Dibromo-2-methyl-6-nitro-1,4-benzoquinone 〔5〕.

The reaction of 6.0g 〔3〕 with a mixed acid consisted of 6.0g of 98% H_2SO_4 and 1.6g of 98% HNO_3 afforded 4.9g of a yellow product, mp 81~112℃. The crude product was recrystallized from ligroin to give 0.3g of 3,5-dibromo-2-methyl-6-nitro-1,4-benzoquinone 〔5〕, yellow leaves, mp 201~202℃. Found: C, 25.75; H, 0.78; N, 4.20%. Calcd for $C_7H_3Br_3NO_4$: C, 25.88; H, 0.93; N, 4.31%.

IR: 1680, 1660, 1590, 1545, 1360, 1300, 1230, 1175, 990, 760, 720, and 680 cm^{-1}.

The mixture of the benzoquinones 〔4〕 and 〔5〕 showed mp 215~217℃, and 〔5〕 was decomposed by refluxing in methanol to give tar.

5. 2,4,6-Tribromo-3-methyl-5-nitrophenol 〔6〕.

A mixture of 10.0g of 〔3〕, 20 ml of HI (d 1.70) and 20 ml acetic acid was refluxed (110℃) for 4 h, diluted, and extracted with benzene. Removal of the solvent from the benzene solution afforded 5.5g (56.8%) of 2,4,6-tribromo-3-methyl-5-nitrophenol 〔6〕, woolly crystals from petroleum ether, mp 153~154℃. Found: C, 21.56; H, 0.95; N, 3.54%. Calcd for $C_7H_4Br_3NO_3$: C, 21.57; H, 1.03; N, 3.59%.

IR: 3400, 1540, 1365, 1180, 950, and 780 cm^{-1}.

NMR ($CDCl_3$): $\delta = 2.62$ (s, 3H, CH_3) and 6.30 (br, 1H, OH; disappeared with D_2O).

6. 3-Methoxy-5-methylaniline〔7〕.

To a mixture of 20g of 〔3〕 and 160 ml of conc HCl, 70g of Zn was added over

a period of 2 h with boiling, and stirring was continued for 6 h. After excess Zn was filtered off, the filtrate was alkalified with NaOH and distilled with steam. The distillate (2 L) was extracted with benzene and removal of the solvent from the extract provided 6.4g (94.1%) of 3-methoxy-5-methylaniline 〔7〕, bp 120～122 ℃/9 mmHg, woolly crystals from 50% methanol or plates from petroleum ether, mp 46～47 ℃ (lit,[4] bp 150 ～ 152 ℃ / 22 mmHg, mp 46～47 ℃). Found : C, 69.98 ; H, 8.31 ; N, 10.10%. Calcd for $C_8H_{11}NO$: C, 70.04 ; H, 8.08 ; N, 10.21%.

IR : 3400, 1595, 1485, 1345, 1200, 1150, 1060, and 820 cm^{-1}.

NMR ($CDCl_3$) : δ=2.25 (s, 3H, CH_3), 3.38 (s, 2H, NH_2 ; disappeared with D_2O), 3.75 (s, 3H, OCH_3), and 6.15 (m, 3H).

Picrate : Yellow needles from ethanol, mp 184.0～184.5℃. Found : C, 46.12 ; H, 3.72 ; N, 15.45 %. Calcd for $C_{14}H_{14}N_4O_8$: C, 45.90 ; H, 3.85 ; N, 15.30%.

A mixture of 2.0g of 〔7〕, 4.0g of acetic anhydride and 10g of acetic acid was stirred at 90 ℃ for 1 h giving 2.2g (84.6%) of 3-methoxy-5-methylacetanilide, needles from 70 % methanol, mp 120 ～ 121 ℃ (lit,[4] mp 110～111 ℃). Found : C, 66.92 ; H, 7.40 ; N, 7.64 %. Calcd for $C_{10}H_{13}NO_2$: C, 67.02 ; H, 7.31 ; N, 7.82%.

IR : 3300, 1665, 1620, 1595, 1560, 1460, 1425, 1370, 1350, 1275, 1200, 1165, 1145, 1070, and 835 cm^{-1}.

NMR ($CDCl_3$) : δ=2.13 (s, 3H, $COCH_3$), 2.27 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 6.50 (br, 1H), 6.85 (br, 1H), 7.07 (br, 1H), and 7.83 (br, 1H, NH ; disappeared with D_2O).

7. Orcinol Monomethyl Ether (3-Methoxy-5-methylphenol) 〔8〕.

A solution of 5.0g of 〔7〕 and 48 ml of 10% H_2SO_4 (d 1.072) in 100 ml water was diazotized by adding a solution of 2.6g of $NaNO_2$ in 20 ml water at 0 ℃. The diazotized solution was slowly added into 200 ml of 3% H_2SO_4 (d 1.020) at 100 ℃ over a period of 40 min with stirring. The mixture was refluxed for 30 min and distilled with steam. The distillate (3 L) was extracted with benzene. From the benzene extract, 3.6 g (72.4%) of orcinol monomethyl ether 〔8〕 was obtained, bp 117～119 ℃/ 6 mmHg, prisms from petroleum ether, mp 62.5 ～ 63.5℃ (lit,[2] bp 89～90 ℃/2 mmHg, 156 ～ 158 ℃ / 25 mmHg ; mp 61 ～ 62 ℃). Found : C, 69.43 ; H, 7.46 %. Calcd for $C_8H_{10}O_2$: C, 69.54 ; H, 7.30 %.

IR : 3350, 1615, 1590, 1500, 1465, 1335, 1300, 1210, 1150, 1060, 830, and 685 cm^{-1}.

NMR ($CDCl_3$) δ=2.20 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 6.28 (br, 3H), and 6.55 (br, 1H, OH ; disappeared with D_2O).

8. Azo Compounds 〔9〕, 〔10〕, and 〔11〕.

A solution of 1.0g of 〔7〕 and 2 ml of conc HCl in 20 ml water was diazotized with 14.8 ml of 0.5N-$NaNO_2$. The diazotized solution was added to a solution of 0.7g of phenol, 1.7 g of 19 % NaOH and 2 g Na_2CO_3 in 20 ml water. The resulting azo compound was filtered, dried and washed with ligroin to give 1.7 g (94.4 %) of 〔9〕,

yellow microcrystals, mp 126～127 ℃. Found : C, 69.21 ; H, 5.68 ; N, 11.42 %. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.40 ; H, 5.83 ; N, 11.56 %.

IR : 3100, 1595, 1500, 1450, 1415, 1335, 1280, 1230, 1150, 1065, 850, and 810 cm^{-1}.

NMR ($CDCl_3$) : $\delta = 2.38$ (s, 3H CH_3), 3.83 (s, 3H, OCH_3), 5.62 (br, 1H, OH ; disappeared with D_2O), 6.83 (br, 1H), 6.89 (d, 2H, J=9 Hz), 7.23 (br, 1H), 7.33 (br, 1H), and 7.84 (d, 2H, J = 9 Hz).

The diazotized solution prepared from 0.5g of [7] was added to a solution of 0.5 g of [8], 0.9 g of 19 % NaOH, and 1.0 g Na_2CO_3 in 10 ml water. The resulting azo compound was filtered, dried and washed with ligroin to give 1.0 g (98.6%) of [10], yellowish brown microcrystals, mp 130～132 ℃. Found : C, 65.20 ; H, 6.34 ; N, 9.78 %. Calcd for $C_{16}H_{18}N_2O_2$: C, 67.11 ; H, 6.34 ; N, 9.78 %.

IR : 3450, 1630, 1600, 1525, 1480, 1440, 1415, 1320, 1220, 1205, 1160, 1080, 1060, and 845 cm^{-1}.

NMR ($CDCl_3$) : δ=2.27 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 5.82 (d, 1H, J=2 Hz), 6.23 (br, 1H), 6.48 (br, 1H), 6.60 (br, 1H), 6.70 (br, 1H), 11.32 (br, 1H, OH ; disappeared with D_2O).

The diazotized solution prepared from 0.4 g of [7] was added to a solution of 0.5 g of β-naphthol, 1.0 g of 16 % NaOH, and 2.0 g Na_2CO_3 in 20 ml water. The resulting azo compound was crystallized from benzene to give 0.8 g (93.8%) of [11], orange prisms, mp 150.0～150.5℃. Found : C, 74.02 ; H, 5.32 ; N, 9.53%. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95 ; H, 5.52 ; N, 9.58 %.

IR : 3450, 1600, 1510, 1445, 1385, 1330, 1295, 1255, 1210, 1125, 1060, 865, 840, and 750 cm^{-1}.

NMR ($CDCl_3$) : δ=2.38 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 6.68 (br, 1H), 6.83 (d, 1H, J=9 Hz), 7.08 (br, 2H), 7.55 (m, 4H), 8.56 (m, 1H), and 16.00 (br, 1H, OH).

9. 2,4,6-Tribromoresorcinol [13].

To a solution of 5.5g (50 m mol) of resorcinol in 200 ml water, 24g (150 m mol) of bromine was added at 10 ℃ for 30 min and stirred for 1 h giving 12.5g (72.0%) of 2,4,6-tribromoresorcinol [13], needles from ligroin, mp 111.5～112.0 ℃ (lit,[5] mp 112 ℃). Found : C, 20.82 ; H, 0.72 %. Calcd for $C_6H_3Br_3O_2$: C, 20.78 ; H, 0.87%.

IR : 3480, 1570, 1460, 1425, 1295, 1220, 1190, 1025, 865, 710, 690, and 660 cm^{-1}.

Tribromoresorcimol [13] was dissolved in aqueous solution of NaOH or $NaHCO_3$. The resulting dark solution was acidified with HCl giving only tar, but no original bromoresorcinol.

10. 4,6-Dibromoresorcinol Dimethyl Ether [14].

To a solution of 5.5g of resorcinol and 23.0g of 19% NaOH in 20 ml water, 13.4 g of dimethyl sulfate was added giving 4.7 g (68.1 %) of resorcinol dimethyl ether, which was also prepared from resorcinol monomethyl ether in 75.4 % yield, bp 102～108℃/24 mmHg.

To a solution of 6.9 g (50 m mol) of resorcinol dimethyl ether in 200 ml water, 24g (150 m mol) of bromine was added at 10℃ and stirred for 1 h giving 14.5g (98.0%) of 4,6-dibromoresorcinol dimethyl ether [14], needles from ligroin, mp 140~141℃ (lit,[6] mp 141 ℃). Found : C, 32.53 ; H, 2.72 %. Calcd for $C_8H_8Br_2O_2$: C, 32.47 ; H, 2.72 %.

IR : 1580, 1485, 1465, 1370, 1290, 1210, 1020, 875, 815, and 685 cm^{-1}.

In this bromination, the same result was also obtained by using 16g (100 m mol) of bromine.

11. 2,4,6-Tribromoresorcinol Dimethyl Ether [16].

To a suspension of 6.2 g (50 m mol) of resorcinol monomethyl ether in 200 ml water, 24 g of bromine was added at 10 ℃ and stirred for 1 h giving 13.5g (74.8 %) of 2,4,6-tribromoresorcinol monomethyl ether [15], needles from ligroin, mp 104~105 ℃ (lit,[7] mp 104~105℃). Found : C, 23.45 ; H, 1.34%. Calcd for $C_7H_5Br_3O_2$: C, 23.30 ; H, 1.40 %.

IR : 3420, 1450, 1435, 1395, 1290, 1215, 1040, 990, 850, 770, 740, and 690 cm^{-1}.

A solution of 18.1g (50 m mol) of [15] and 22g of 10% NaOH in 50 ml water was treated with 6.6 g of dimethyl sulfate giving 16.5 g (88.0%) of 2,4,6-tribromoresorcinol dimethyl ether [16], needles from ligroin, mp 68~69 ℃ (lit,[8] mp 68~69 ℃). Found : C, 25.92 ; H, 1.88 %. Calcd for $C_8H_7Br_3O_2$: C, 25.63 ; H, 1.88 %.

IR : 1455, 1410, 1365, 1220, 1060, 990, 925, 860, 770, 750, 710, 680, and 625 cm^{-1}.

12. 2,4,6-Tribromo-5-nitroresorcinol Dimethyl Ether [17].

To a mixed acid prepared from 10.0g of 98 % H_2SO_4 and 2.8g (44 m mol) of 98 % HNO_3, 4.0 g (11 m mol) of [16] was slowly added at −10 ℃ (30 min) and then stirred for 2 h. After stirring at 0 ℃ for 1 h, the reaction mixture was poured into an ice water giving 2.0g (44.6%) of 2,4,6-tribromo-5-nitroresorcinol dimethyl ether [17], prisms from methanol, mp 126.0 ~ 126.5 ℃ (lit,[9] mp 126 ℃). Found: C, 22.76 ; H, 1.26 ; N, 3.26 %. Calcd for $C_8H_6Br_3NO_4$: C, 22.89 ; H, 1.44 ; N, 3.34 %.

IR : 1540, 1450, 1380, 1360, 1080, 1005, and 930 cm^{-1}.

To a mixture of 4.0 g of [17], 40 ml conc HCl, 10 ml benzene and 40 ml water, 6.4 g Zn was added at room temperature during 5 h. After the mixture was stirred at 20 ℃ for 15 h, from the benzene layer 2.7g (72.7%) of 2,4,6-tribromo-3,5-dimethoxyaniline [18] was obtained, needles from methanol, mp 105~106 ℃. Found : C, 25.74 ; H, 2.17 ; N, 3.58 %. Calcd for $C_8H_8Br_3NO_2$: C, 24.64 ; H, 2.07 ; N, 3.59 %.

IR : 3410, 3300, 1600, 1580, 1545, 1450, 1410, 1390, 1345, 1205, 970, 925, 745, 705, and 685 cm^{-1}.

NMR ($CDCl_3$) : δ=3.85 (s, 6H, two OCH_3), 4.77 (br, 2H, NH_2 ; disappeared with D_2O).

In this reaction, [17] was not reduced in an absence of benzene and when [17] was treated as described in section 6 none of the reduction products contained traces

of tar.

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References

1) R. M. Anker and A. H. Cook, *J. Chem. Soc.*, 1945, 311.

2) a) G. I. Feutrill and R. N. Mirrington, *Tetrahedron Lett.*, 1970, 1327.

b) R. N. Mirrington and G. I. Feutrill, *Org. Synth.*, 53, 90 (1973).

3) K.Adachi, *Bull. Chem. Soc. Jpn.*, 46, 688 (1973).

4) B. D. Haworth and A. Lapworth, *J. Chem. Soc.*, 123, 2982 (1923).

5) L. C. Raiford and Heyl, *J. Am. Chem. Soc.*, 44, 215 (1922).

6) M. Kohn and L. Steiner, *J. Org. Chem.*, 12, 30 (1947).

7) L. C. Raiford and J. H. Scott, *J. Org. Chem.*, 2, 213 (1937).

8) H. A. Torrey and W. H. Hunter, *J. Am. Chem. Soc.*, 33, 194 (1911).

9) Jackson and Warren, *J. Am. Chem. Soc.*, 13, 188 (1891).